


 Cite this: *RSC Adv.*, 2025, 15, 21785

# Advanced electrochemical treatment of tetracycline-contaminated water using Pt/Ti electrodes†

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The electrochemical mineralization of tetracycline in chloride aqueous solutions using Pt/Ti anodes has been investigated. The mineralization process, oxidation efficiencies and oxidation products were characterized by UV-visible spectroscopy and HPLC-MS. Tetracycline oxidation efficiencies are  $97 \pm 2\%$  in 0.64 wt% HCl and  $85 \pm 3\%$  in 0.64 wt% NaCl within 15 minutes of electrolysis. UV-visible spectroscopy confirmed the degradation of the antibiotic's  $\pi$ -conjugated electron system and allowed the identification of active species (*i.e.*, hydrogen peroxide and dissolved chlorine) that can potentially degrade tetracycline. The formation of these active species is due to the high positive potential of the Pt/Ti anode during electrolysis. HPLC-MS studies show the intensity of the tetracycline peak to gradually decrease during electrolysis, indicating its oxidation. Peaks corresponding to oxidation intermediates with a molecular weight above 70 were not detected, which indicates the absence of oxidation products with higher molecular mass. During electrochemical oxidation of tetracycline, small amounts of formaldehyde are formed, but its concentration can be brought to an acceptable level by diluting the solution. In negative mode, chlorate ions were detected in the NaCl solutions, which are likely formed from the stepwise oxidation of chloride ions; however, this phenomenon is not observed in HCl solutions.

 Received 15th April 2025  
 Accepted 17th June 2025

DOI: 10.1039/d5ra02632f

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## Introduction

The extensive use of antibiotics in agriculture and healthcare industries has contributed to the emergence of antibiotic-resistant microorganisms, presenting a growing threat to global health.<sup>1–4</sup> One of these antibiotics is tetracycline, a broad-spectrum agent that exhibits activity against a wide range of Gram-positive and Gram-negative bacteria.<sup>5</sup>

The use of antibiotics during the treatment of SARS-CoV-2 has led to the significant presence of unmetabolized species in wastewater.<sup>6,7</sup> These antibiotics enter the sewage system, and elevated levels have been detected in surface and groundwater.<sup>8–12</sup> Antibiotics are widely used in livestock and poultry farming for preventive and supportive treatments.

Waste containing antibiotics is often disposed-of improperly, leaching into water.<sup>13–18</sup>

Studies on antibiotic removal from wastewater have revealed that conventional methods using hydrogen peroxide, ozone, and hypochlorite ions have low mineralization efficiency.<sup>19–22</sup> Advanced oxidation processes (AOPs), which generate highly reactive radicals, are considered the most promising methods for the mineralization of antibiotics.<sup>19,22–25</sup> The use of AOPs faces challenges such as complex system designs, high reagent consumption and operational costs.<sup>26–29</sup> An alternative approach to AOPs is the oxidation using ferrates, which offers efficient removal at a relatively low cost.<sup>30–33</sup> AOPs are effective for antibiotics at concentrations below  $2 \text{ mg L}^{-1}$  but require initial treatment for higher concentrations.<sup>20,22–25</sup> Supercritical water oxidation, another potential treatment, is hindered by its high operational costs and complexity.<sup>27,34,35</sup> Electro-oxidation provides a simple and cost-effective method for treating highly concentrated pollutants.<sup>36–39</sup>

Concerning tetracycline, AOPs can achieve up to 99% mineralization for concentrations between 0.1 and  $1.0 \text{ mg L}^{-1}$  but treatments for higher concentrations are lacking. Electro-oxidation has shown promise for tetracycline removal, with residual pollutants easily removed by subsequent AOPs.<sup>40,41</sup> Several studies have explored electro-oxidation of tetracycline, employing various anode materials such as Pb/PbO<sub>2</sub>, Nb/BDD,

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 † Electronic supplementary information (ESI) available: See DOI: <https://doi.org/10.1039/d5ra02632f>


and Ti/RuO<sub>2</sub>-IrO<sub>2</sub>.<sup>42–48</sup> So far, complete mineralization of tetracycline has not been achieved, and the nature of the oxidation products remains underexplored. The presence of chloride ions during electrolysis generates active species that may enhance oxidation.<sup>47</sup>

Here, we explore the electrochemical oxidation of tetracycline using Pt/Ti anodes in aqueous chloride media, assess the degree of mineralization, and identify the oxidation products.

## Experimental section

### Materials

Tetracycline (Tyumen Chemical-Pharmaceutical Plant), HCl (12 M, reagent grade, Reachim), NaCl (reagent grade, Reachim) and deionized water ( $R > 18 \text{ M}\Omega \text{ cm}$ , TOC < 3 ppb) were used. The 8 wt% HCl solution was prepared by diluting 12 M HCl.

### Electrochemical methods

Electro-oxidation experiments were conducted under galvanostatic conditions ( $I = 0.1\text{--}0.4 \text{ A}$ ) using a DAZHENG PS-305D PC Power Supply. The anolyte (120 mL) contained tetracycline dissolved in HCl or NaCl solution, and the catholyte (40 mL) contained all components except tetracycline. Pt/Ti anodes (YUNCH, China),<sup>47</sup> ( $S_{\text{geom}} = 10 \text{ cm}^2$ ) and Ti cathodes were used. For Pt/Ti anodes, the manufacturer indicates<sup>48</sup> a platinum layer thickness of 0.5–10  $\mu\text{m}$  (platinum loading of 1–20  $\text{mg cm}^{-2}$ ) and that thermal decomposition of platinum salts on titanium substrate was used to prepare the electrode. Our ICP-MS analysis, performed after dissolution of the active layer of anode in *aqua regia*, showed an average platinum loading of  $\sim 5 \text{ mg cm}^{-2}$ .

The choice of Pt/Ti anodes for indirect tetracycline electro-oxidation is due to their commercial availability. Moreover, efficient generation of active oxygen and chlorine containing species is only possible at high anodic potentials. Oxygen evolution begins at  $E > 1.7 \text{ V}$  (RHE) on Pt/Ti electrodes and dissociative adsorption of organic molecules further causes a positive shift in the potential.

Ti/PbO<sub>2</sub> electrodes are also characterized by positive oxygen evolution potentials. However, Pb(II) ions are toxic, and their formation, which can occur during current interruptions, is from an environmental and health point of view unsustainable. The most positive potentials can be reached using boron-doped diamond (BDD) anodes; however, this material is scarce and has not yet been commercialized.

The Ti<sub>4</sub>O<sub>7</sub> anodes, exhibit strong oxidation performance for the degradation tetracycline.<sup>47,49,50</sup> These electrodes exhibit good conductivity, but they can undergo degradation over time accompanied by an increase in the resistance of the interphase boundary.<sup>51</sup> This drawback can be addressed using complex preparation methods, e.g. deposition of an Ir@IrO<sub>x</sub> layer.

Polarization measurements were conducted in a standard three-electrode cell. The working electrode potential was referenced against a saturated Ag/AgCl electrode. All potentials were calculated to a reversible hydrogen electrode (RHE) in the same solution. A digital potentiostat IPC-MS (Volta) was used for

measurements under potentiodynamic conditions. Solutions were bubbled with argon gas for 30 minutes prior experiments.

### Microscopic and diffraction methods

Surface morphology was analyzed using a Thermo Fisher Scientific Quattro S SEM, equipped with secondary electron, backscattered electron, and energy-dispersive X-ray detectors (Bruker SDD). SEM images were recorded under high vacuum conditions with currents ranging from 87 pA to 200 nA and accelerating voltages between 2 kV and 30 kV. The phase composition was examined by powder X-ray diffraction using a Bruker D8 ADVANCE diffractometer with Cu K $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ).

### Analytical methods

HPLC-MS analysis was performed using a Dionex Ultimate 3000 chromatograph (Thermo Fisher Scientific) coupled with an Orbitrap Elite Hybrid ion trap mass spectrometer (Thermo Fisher Scientific). Chromatographic separation was conducted on a Shim-pack GIST-HP C18-Aq column (150  $\times$  3 mm, 3  $\mu\text{m}$ ) with a mobile phase consisting of 0.1% formic acid in deionized water and 0.1% formic acid in isopropyl alcohol at a flow rate of 0.3  $\text{mL min}^{-1}$ . The analysis time was 30 minutes, and mass spectra were obtained in both positive and negative modes over the 103–1500  $m/z$  range. Samples (1 mL) were taken at different electrolysis times, mixed with NaOH (200 mL, 0.2 M), and centrifuged.

Chemical oxygen demand (COD) was measured using a photometric method. Potassium dichromate and sulfuric acid were added to the sample, and silver sulfate was used to remove chloride ions. After heating at 150  $^{\circ}\text{C}$  for 2 hours, absorbance was measured at 400 nm (COD 10–160  $\text{mgO}_2 \text{ L}^{-1}$ ) or 600 nm (COD 160–800  $\text{mgO}_2 \text{ L}^{-1}$ ).

UV-visible spectra were recorded using a SF-2000 digital spectrophotometer. The concentration of tetracycline was monitored using a photoelectric colorimeter (CPC-3) at 360 nm. The absorption spectrum of the tetracycline displays two distinct bands at 276 and 360 nm (Fig. S1†). Formaldehyde was identified using a colorimetric method.<sup>52</sup>

Chlorate ions were detected by ion-exchange chromatography using ion chromatograph dionex ISC-3000 in reagent-free suppressor IC mode. Gradient (NaOH) elution was used.

### Characterization of the electrodes

Electrochemical treatment of aqueous tetracycline solutions was performed using Pt/Ti anodes. The cyclic voltammogram (Fig. S2†) at the Pt/Ti anode reveals hydrogen, double-layer, and oxygen regions typical for platinum electrodes. The hydrogen region is asymmetric, indicating a hydrogen spillover effect. Platinum oxide formation begins around 0.8 V, a behavior characteristic of platinum electrodes.

The morphology of Pt/Ti anodes was analyzed by SEM. The surface of Pt/Ti electrodes (Fig. S3†) contains platinum clusters composed of nanoparticles. During electrolysis, these platinum nanoparticles serve as active sites for the formation of reactive chlorine and oxygen species. The SEM images were taken after



1000 hours of electrolysis, demonstrating the nanoparticles to remain stable under these conditions. The powder X-ray diffraction pattern of the Pt/Ti electrodes (Fig. S4†) shows reflections corresponding to the platinum phase. Using the Scherrer equation, the average size of the platinum nanoparticles was estimated to be  $\sim 20$  nm.

Carbon monoxide monolayer desorption was performed to determine the electrochemically active surface area (EASA) of the electrode (Fig. S5†),<sup>53,54</sup> a coefficient of  $0.42 \text{ mC cm}^{-2}$  was used for the calculation. The potential region for CO desorption and the shape of the desorption peak are characteristic of platinum catalysts. The EASA ( $25.0 \text{ cm}^2$ ) remains constant after electrolysis under oxygen evolution, highlighting the stability of the electrode material.

## Results and discussion

Using tetracycline in its commercial form simulates practical conditions, as both active ingredients and auxiliary agents are present in wastewater. During electrolysis, chlorine and oxygen species may oxidize the auxiliary agents instead of tetracycline, so studying tetracycline in its commercial form is essential before applying wastewater treatment methods.

A tetracycline-LekT tablet containing tetracycline hydrochloride ( $\sim 1$  g) was crushed in an agate mortar, weighed, and dissolved in 20 mL of either 8 wt% HCl or 8 wt% NaCl. The solution was then diluted to 250 mL with DI water. Chloride-containing media were found to produce the best results for tetracycline oxidation.<sup>47,55</sup> Electro-oxidation was performed in 0.64 wt% solutions of HCl (initial pH = 0.8) or sodium chloride (initial pH  $\sim 6.0$ ).

In 0.64 wt% HCl, anodic processes occur above 1.3 V (Fig. 1a), primarily involving oxygen and chlorine evolution. The introduction of tetracycline in the solution significantly inhibits these anodic reactions. It is likely that tetracycline molecules adsorb *via* O atoms onto the platinum surface inhibits anodic processes. A similar phenomenon, where the oxidation of  $\text{Br}^-$  ions is inhibited by small amounts of phenol, has been reported.<sup>56</sup>

The shift toward positive potentials promotes the formation of active oxygen and chlorine species, which may contribute to the complete mineralization of tetracycline. A similar effect was observed in NaCl solutions (Fig. 2b). Due to oxygen evolution, the near-anodic layer becomes acidic and thus anodic processes in both HCl and NaCl solutions occur at similar potentials.

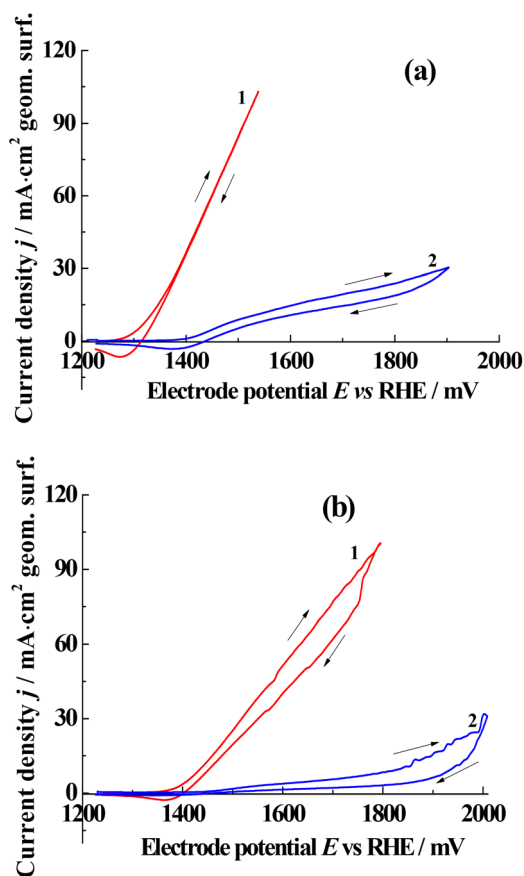


Fig. 1 Potentiodynamic ( $5 \text{ mV s}^{-1}$ ) polarization curves in 0.64 wt% HCl (a) and 0.64 wt% NaCl (b) solutions. 1 – blank solution of HCl (red curve) and NaCl (blue curve), 2 – tetracycline ( $1.09 \text{ mg L}^{-1}$ ).

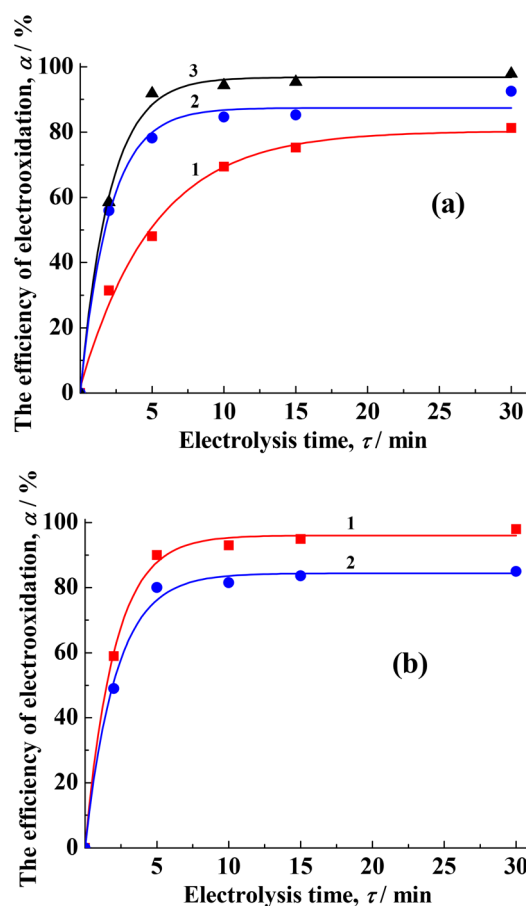


Fig. 2 (a) Tetracycline electrooxidation efficiency as a function of electrolysis time for different initial concentrations ( $c_{\text{in}}$ ,  $\text{mg L}^{-1}$ ) in 0.64 wt% HCl: 1 = 80 (in red), 2 = 40 (in blue), 3 = 15 (in black). (b) Oxidation of tetracycline ( $c_{\text{in}} = 20 \text{ mg L}^{-1}$ ) in 0.64 wt% HCl (1, in red) and 0.64 wt% NaCl (2, in blue) solutions.  $I = 0.4 \text{ A}$ ,  $j = 0.04 \text{ A cm}^{-2}$ .



The electro-oxidation of tetracycline in HCl solution is highly efficient. When the initial concentration of tetracycline is  $15 \text{ mg L}^{-1}$ , the oxidation yield reaches  $97 \pm 2\%$  within 15 minutes of electrolysis (Fig. 2a). At higher concentrations of tetracycline ( $80 \text{ mg L}^{-1}$ ), complete oxidation is not achieved in 30 minutes (yield:  $81 \pm 3\%$ ). The energy consumption for tetracycline removal calculated from the values of current, cell voltage and duration of electrolysis, was estimated to be  $\sim 0.3 \text{ kW h}$  per gram of tetracycline in acidic media.

The efficiency of tetracycline electro-oxidation is slightly dependent on solution acidity, showing oxidation rate of ( $97 \pm 2\%$ ) in 0.64 wt% HCl and ( $85 \pm 3\%$ ) in 0.64 wt% NaCl (Fig. 2b). These values are comparable to that reported for oxytetracycline,<sup>47</sup> where 96% of oxytetracycline was oxidized after 3 hours of electrolysis using Pt/Ti anodes in 40 mM NaCl solution. This is likely due to the acidification of the near-anode region caused by oxygen evolution, the primary anodic process in both solutions. The pH of the anolyte in NaCl decreases to 3.0 within 3 minutes of electrolysis, reaching 2.5 after 10 minutes and remaining stable. Meanwhile, the pH of the catholyte solution increases to 12.5.

The degradation of tetracycline was studied by UV-visible spectroscopy during the electrochemical treatment. Bands at 276 and 360 nm (Fig. 3) of the initial solution are due to  $\pi$ -conjugated electron system (C=C and C=O bonds). These bands disappear after 10 minutes of electrolysis, which indicates the degradation of tetracycline and the absence of accumulation in significant quantities of substances containing conjugated  $\pi$ -bonds, primarily quinones.<sup>49</sup> It is proposed that active chlorine and oxygen species generated at the anode play an active role in the degradation process.

UV-visible measurements support this hypothesis, as the spectra of tetracycline in 0.64 wt% HCl during electrolysis (Fig. 4) show the appearance of bands at 223 nm and 350 nm respectively consistent with the formation of hydrogen peroxide<sup>57,58</sup> and dissolved chlorine.<sup>59</sup> It is likely that active

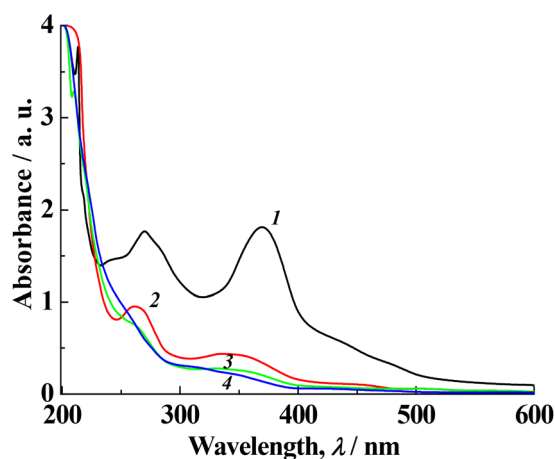


Fig. 3 UV-visible spectrum of tetracycline in 0.64 wt% HCl as a function of electrolysis time. Initial concentration of tetracycline  $c_{\text{in}} = 80 \text{ mg L}^{-1}$ ,  $j = 0.02 \text{ A cm}^{-2}$ ,  $I = 0.2 \text{ A}$ . Time of electrolysis (min): 1 = 0 (in black), 2 = 5 (in red), 3 = 10 (in green), 4 = 20 (in blue).

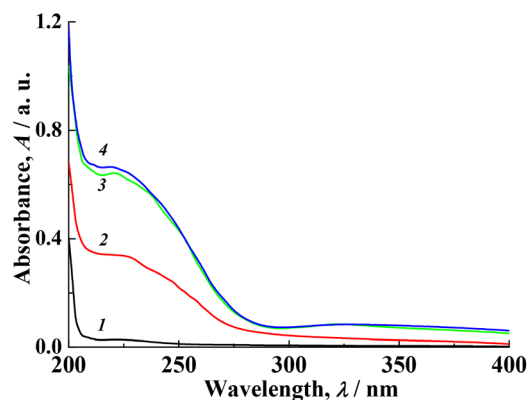


Fig. 4 UV-visible spectra of a solution of HCl (0.64 wt%) during electrolysis (Pt/Ti anode,  $I = 0.2 \text{ A}$ ,  $j = 0.02 \text{ A cm}^{-2}$ ). Time of electrolysis (min): 1 = 0, 2 = 5, 3 = 10, 4 = 15.

species, e.g.  $\cdot\text{Cl}$  and  $\cdot\text{OH}$ , generated during electrolysis degrade the tetracycline molecules. Theoretically, the contribution of free radicals could be distinguished by radical quenching experiments. However, radical scavengers undergo dissociative chemisorption on platinum anodes,<sup>60,61</sup> which inhibits electrode reaction and affects the experiment results.

XPS analysis (Fig. S6<sup>†</sup>) of the Pt/Ti electrode after tetracycline oxidation, showed the presence of platinum metal, oxygen, chlorine, and carbon. The carbon content decreases after ion etching at a depth of 5 nm and the C1 peak suggests the presence of carbon-containing contaminants.

Tetracycline oxidation efficiency is comparable in both acidic and neutral solutions. Due to the oxygen evolution, the near-electrode region is more acidic than the bulk solution. Since tetracycline degradation occurs in this region, where active oxygen and chlorine species are concentrated, the oxidation rate in both acidic (pH = 2–3) and neutral (pH = 5–6) solutions are comparable (Fig. 5). Initially, the oxidation rate differs by a factor of 1.3 as the near-electrode acidity is still adjusting. After 10 minutes of electrolysis, the residual

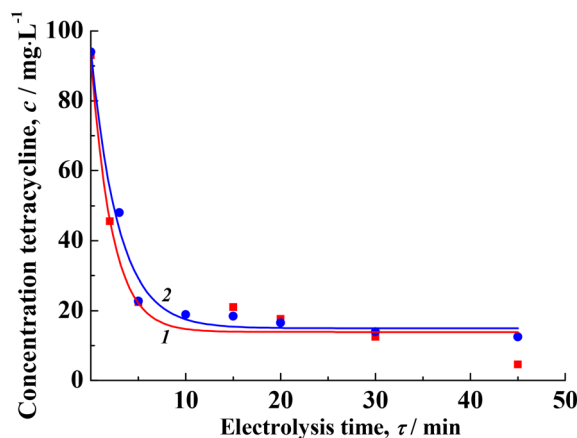


Fig. 5 Tetracycline concentration as a function of electrolysis time in (1) 0.64 wt% HCl (in blue) and (2) NaCl (in red) solutions.  $I = 0.4 \text{ A}$ ,  $j = 0.04 \text{ A cm}^{-2}$ .



**Table 1** Chemical oxygen demand values during the electrolysis of 0.64 wt% NaCl containing 80 mg L<sup>-1</sup> tetracycline.  $l = 0.4$  A,  $j = 0.04$  A cm<sup>-2</sup> after 15 min and 30 min.  $l = 0.2$  A,  $j = 0.02$  A cm<sup>-2</sup>

Time (min)	0 (Initial)	15	30
COD (mg <sub>O<sub>2</sub></sub> L <sup>-1</sup> )	313	285	91

tetracycline concentrations in both solutions approach values (17–20 mg L<sup>-1</sup>, Fig. 5) corresponding to its removal by 80–85%.

Chemical oxygen demand value indicates the amount of oxygen needed for oxidation of organic substances in an aqueous solution. Its sharp decrease in the first 30 minutes of electrolysis (Table 1) indicates a high degree of tetracycline mineralization to products, which cannot be oxidized by dichromate ions. Value of 91 mg<sub>O<sub>2</sub></sub> L<sup>-1</sup> may be due to the presence of residual organic metabolites after electrochemical treatment; these metabolites were identified by HPLC/MS (*vide infra*).

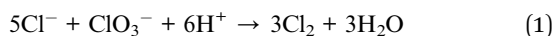
The degradation of tetracycline is a complex process and the formation of toxic intermediates during electrochemical treatment is problematic. Possible intermediates (*e.g.* quinones) of tetracycline oxidation at Ti/Ti<sub>4</sub>O<sub>7</sub> anodes were reported<sup>49</sup> and their toxicity was assessed using a standard water test method based on the bioluminescence of *Vibrio fischeri* bacteria.

To monitor tetracycline oxidation, mass spectra in both positive and negative ions were recorded in NaCl solution. Results (Fig. 6 and Table 2) show that tetracycline (retention time of 11.64 minutes) was detected in the mass spectra of the initial solutions, in both positive and negative modes.

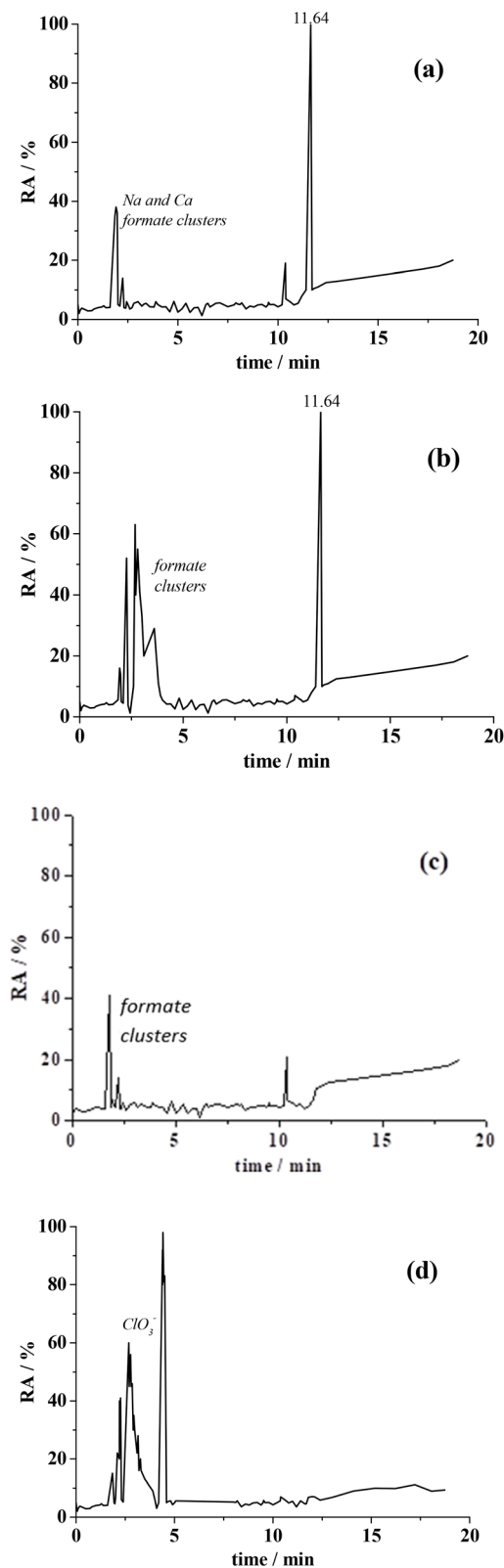
In positive mode, the mass spectrum shows a peak at  $m/z = 445.16$  corresponding to the protonated form of tetracycline (Fig. 6)<sup>62</sup> while in negative mode, tetracycline, in its deprotonated form appears at  $m/z = 443.14$ , a pre-peak at 10.94 minutes is likely attributed to a tetracycline structural isomer, doxycycline,<sup>63</sup> as its molecular peak matches at  $m/z = 445.16$  (positive mode).

The intensity of the tetracycline peak gradually decreases during electrolysis, indicating its oxidation. Peaks corresponding to possible oxidation intermediates (*e.g.* quinones)<sup>49</sup> were not detected (Fig. 6), suggesting that contaminants with a molecular weight above 70 were not produced during oxidation. In negative mode, chlorate ions (ClO<sub>3</sub><sup>-</sup>,  $m/z = 83, 85$ , intensity ratio 3 : 1) were detected and likely formed during the stepwise oxidation of chloride.<sup>50</sup> By analogy with sodium acetate cations (*i.e.*, Na<sup>+</sup>(CH<sub>3</sub>COO-Na<sup>+</sup>)<sub>*n*</sub>) the formula M<sup>+</sup>(HCOO-M<sup>+</sup>)<sub>*n*</sub> (M = Na, Ca) is proposed.<sup>64</sup>

The formation of ClO<sub>3</sub><sup>-</sup> ions in neutral NaCl solutions raises toxicity concerns. After electrolysis in 0.5 M NaCl, a relatively high chlorates concentration (~28 ppm) was measured by ion-exchange chromatography. The formation of chlorate ions does not occur in acid solutions (Fig. S7†) due to their reaction with chloride:



Therefore, electrolysis in HCl solutions prevents the formation of chlorates.



**Fig. 6** Monitoring of tetracycline (10 mg L<sup>-1</sup>) oxidation ( $l = 0.2$  A,  $j = 0.02$  A cm<sup>-2</sup>) in 0.64 wt% NaCl by HPLC-MS. Chromatograms of initial solution in positive (a) and negative mode (b); chromatograms after 30 min of electrochemical treatment in positive (c) and negative mode (d).



**Table 2** Retention time,  $m/z$ , intensity and attribution of species found by HPLC-MS during the electrooxidation of tetracycline (10 mg L<sup>-1</sup>) in 0.64 wt% NaCl.  $I = 0.2$  A,  $j = 0.02$  A cm<sup>-2</sup>

Mode	Retention time (min)	$m/z$	Intensity (%)	Species
Negative	1.90–3.00	515, 433 and others	80	Clusters of sodium and calcium cations with formate anions <sup>64</sup>
Negative	4.37	83, 85	15	ClO <sub>3</sub> <sup>-</sup>
Negative	11.65	443.16	<5	Tetracycline
Negative	10.94	443.16	<1	Doxycycline
Positive	1.94–2.25	515 and others	90	Clusters of sodium and calcium cations with formate anions <sup>64</sup>
Positive	11.64	445.16	10	Tetracycline
Positive	10.94	445.16	<1	Doxycycline

The concentration of formaldehyde determined after the oxidation (30 min) of tetracycline (10 mg L<sup>-1</sup>) for two current values (0.43(2) mg L<sup>-1</sup> at 0.2 A and 0.71(3) mg L<sup>-1</sup> at 0.5 A) is above the maximum allowable concentration for water bodies used in fisheries (0.25 mg L<sup>-1</sup> in the Russian Federation, 0.05 mg L<sup>-1</sup> in the United Kingdom<sup>65</sup> and 0.11 mg L<sup>-1</sup> in the United States<sup>66</sup>). The authors note that reaching drinking water concentration standards is unnecessary, as the water will be discharged into the sewer system, where it will be further diluted. Formaldehyde levels could be reduced to regulatory values using sorption technologies such as adsorption on kaolin and bentonite.<sup>67</sup>

## Conclusions

In summary, the electrochemical mineralization of aqueous chloride solutions containing high concentrations of tetracycline was successfully achieved using Pt/Ti anodes. The efficiency values found for the electro-oxidation of tetracycline solutions (>85%) is comparable to other method (*e.g.* 95% for photo-oxidation).<sup>68</sup> Our studies show that the efficiency of commercial Pt/Ti anodes for tetracycline oxidation is comparable with Ti<sub>4</sub>O<sub>7</sub> (~95%) and comparable to Ti/RuO<sub>2</sub>-IrO<sub>2</sub>@Pt anodes (~90%). The adsorption of tetracycline molecules, and their fragments, on the platinum surface shifts the anode potential to more positive values, facilitating the formation of active oxygen and chlorine species. These species interact with tetracycline, leading to the breakdown of its  $\pi$ -conjugated electronic system. In the presence of chloride ions, tetracycline removal is nearly identical in both acidic and neutral solutions due to the acidification of the anolyte from the oxygen evolution reaction. HPLC-MS analysis of tetracycline oxidation showed that organic intermediates do not accumulate significantly during electrolysis. Chlorate ions, doxycycline and clusters of sodium and calcium cations with formate anions were detected and likely formed during the stepwise oxidation process. One concern about the method is the formation of formaldehyde with concentration above regulatory values. Current work focus on reducing these values using sorption technologies and results will be reported in due course.

## Data availability

The data supporting this article have been included as part of the ESI.†

## Author contributions

N. A. I. – experimental work. E. N. K. – experimental work, methodology. V. V. K. – methodology, writing. E. A. F. – experimental work, writing. A. V. P. – chromatograph mass spectrometry, identification of metabolites. Y. V. T. – chromatograph mass spectrometry, identification of metabolites, analytical experiments. F. P. – writing – review & editing. K. E. G. – methodology, evaluation of experimental results. Y. M. A. – experimental, financial support. A. V. K. – material support for experiments.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

The work was supported by the Ministry of Science and Higher Education RF.

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